RELATIONSHIP OF STRUCTURAL PHASE TRANSFORMATIONS AND PROPERTIES OF SOL-GEL FILMS IN THE Bi_2O_3 – TiO_2 – Fe_2O_3 SYSTEM

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It is shown that the structure and properties of gel-sol oxide films depend on the total mass content of film-forming oxides in the solution and are determined by the different degrees of nonequilibrium of the physicochemical processes. The existence of quite clear relationships between the solution viscosity, the specifics of the microstructure, and certain properties of the film is established.

The present paper investigates ternary oxide coatings of the Bi_2O_3 – TiO_2 – Fe_2O_3 system. The compositions of the films and the experimental conditions were identical to those described in [1], except for two items: the film-forming solution (FFS) deposited on the glass had a total oxide content equal to 5%; the chemical resistance of the coatings was evaluated with respect to a 0.1 N hydrochloric acid solution (duration of exposure at room temperature 30 min).

Table 1 shows results of measurements of the viscosity of FFS with a total mass content of the film-forming oxides equal to 2.5% (series A) and 5% (series B) and properties of coatings based on these FFS.

The FFS viscosity varies in the range of 2.281 – 2.880 mm^2/sec. This is higher than for identical solutions of series A and agrees with the Einstein equation [2].

Photomicrographs of varying magnification make it possible to evaluate the microstructure and submicrostructure of the films of series B (Fig. 1a).

The total mass content of the film-forming oxides in the solution has a significant effect not only on its viscosity but also on the properties of the sol-gel film. The refractive index varies ambiguously: it is higher in film 1, equal in films 2 – 4 and 6, and lower in films 5 and 7 than in analogous coatings of series A. This is probably due to porosity variation: a decrease in the porosity fosters an increase in the refractive index, and increased porosity, conversely, reduces this index [3]. An increase (within reasonable limits) in the solution concentration decreases the coating porosity [3], and the occurrence of batch stones has the opposite effect, since film structure is loosened in this case.

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TABLE 1

| Series	FFS viscosity, mm^2/sec	Molar content of Bi_2O_3 in the film, %	Distribution confidence interval of				
			refractive index	specular-reflection coefficient, %	microhardness, MPa	chemical resistance, %, to the action of	
						HCl	H_2O
1A	2.054	10	2.060 – 2.050	34.4 – 33.2	6792 – 6534	–	14 7
1B	2.519	–	2.176 – 2.104	39.6 – 30.9	6457 - 6103	5 – 3	–
2A	2.079	20	2.150 – 2.110	32.2 – 32.0	6461 - 6291	.	54 47
2B	2.576	–	2.196 – 2.139	41.2 – 34.7	7116 - 6766	23 – 16	–
3A	2.045	30	2.160 – 2.150	35.6 – 32.4	6489 - 6336	–	11 – 5
3B	2.281	–	2.204 2.116	39.4 - 37.8	6732 - 6380	11 – 4	-
4A	2.087	40	2.100 – 2.060	36.7 – 33.7	6233 - 6073	–	52 – 37
4B	2.298	–	2.121 – 2.062	34.5 -- 34.3	6730 - 6384	32 – 12	–
5A	2.087	50	2.150 – 2.110	34.1 – 31.3	6104 - 5972	–	24 – 5
5B	2.850	–	2.093 – 1.997	31.9 – 30.5	6661 - 6265	43 – 20	–
6A	2.054	60	2.210 – 2.110	32.0 -- 31.6	6343 – 6123	–	15 - 10
6B	2.880	–	2.231 – 1.921	29.5 – 29.3	6441 – 6113	40 – 15	–
7A	2.155	70	2.070 – 1.930	27.3 – 26.3	5859 – 5719	–	9 – 0
7B	2.800	–	1.727 – 1.547	21.7 – 21.1	6555 – 6178	8 – 2	–
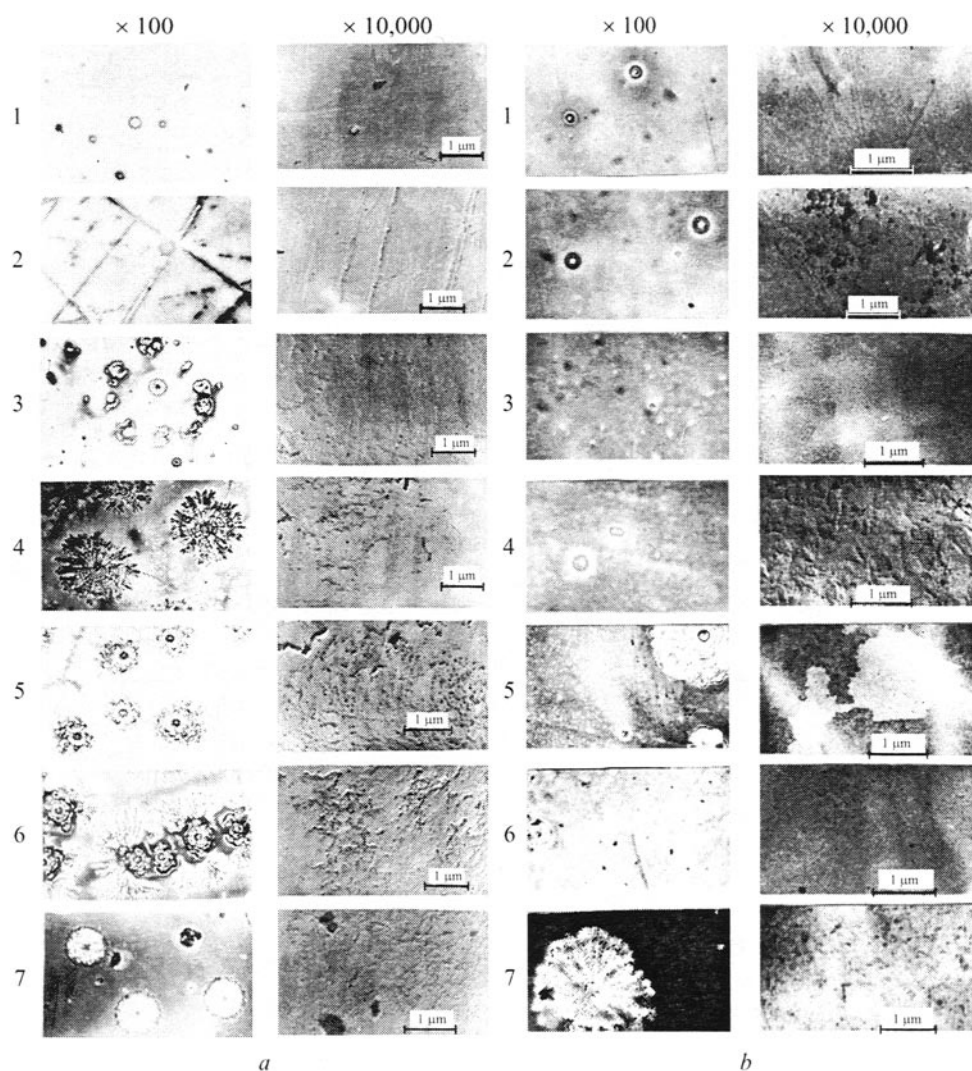
Fig. 1. Films of series B (*a*) and A (*b*) made of 2-day-old solutions.

In comparing the photomicrographs (× 100) shown in Fig. 1, it can be seen that the capacity for stone formation is shifted to the region of compositions with a lower molar content of Bi_2O_3: 30% instead of 50% in the coatings of series A. The main reasons are a decrease in the pH and an increase in the electrolyte content in the solution as its concentration increases. This intensifies the propensity of the sol particles for agglomeration.

Similar phenomena determine the value of the specular-reflection coefficient: the occurrence and/or size (or number) increase size of inclusions that facilitate light scattering decrease the reflection coefficient, and decreased porosity of the coating, on the other hand, increases this coefficient [3]. That is why the reflection coefficient is higher in the first three coatings and is lower in the rest of the coatings than that of identical coatings in series A.

The microhardness and chemical resistance of films belonging to the same film-forming system are largely determined by their submicrostructure. The maximum microhard-

ness in series B is registered in film 2. According to the electron-microscopy data (Fig. 1*a*), the structure of this film contains flagellate formations, which are presumably responsible for the increased microhardness. In the film of the same composition prepared from a solution with a lower mass content of the film-forming oxides (series A), no flagellate formations were identified (Fig. 1*b*), and therefore, its microhardness is significantly lower. Coatings 2, 4, 5, and 7 in series B also have a higher microhardness compared to identical films in series A, which is presumably related to the presence of chain-shaped submicroinclusions of varying length, which are absent in coatings of the same composition in series A. Within the experimental-error limits the microhardness of films 3 and 6 does not depend on the mass content of the film-forming oxides in the solution, and the microhardness of coating 1 in series B is lower than that of the similar coating in series A. This is accounted for by the presence of flagellate formations in the latter coating.

TABLE 2

Sample	Molar content of Bi_2O_3 in the film, %	X-ray phase analysis data for powders obtained from FFS, arb. units	
		series A	series B
1	10	BiOCl – 29, FeCl$_2 \cdot 4H_2O$ – 31	BiOCl – 107
2	20	BiOCl – 78, FeCl$_2 \cdot 4H_2O$ – 0 – 9	BiOCl – 117, FeCl$_2 \cdot 2H_2O$ – 48
3	30	BiOCl – 121, spinel phase* – traces	BiOCl – 17, FeCl$_2 \cdot 2H_2O$ – 32, FeCl$_2 \cdot 4H_2O$ – 31
4	40	BiOCl – 137, spinel phase – 27	BiOCl – 54, mFeCl$_2 \cdot n$H$_2$O – 48
5	50	BiOCl – 101, spinel phase – traces	BiOCl – 252
6	60	BiOCl – 122, spinel phase – traces	BiOCl – 320
7	70	BiOCl – 142	BiOCl – 415

* Solid solutions between Fe_2O_3 and iron titanate with the common formula xFe$_2$O$_3 \cdot (1 - x)$Fe$_2$TiO$_3$ and a spinel structure were identified in the FeO – Fe$_2$O$_3 \cdot$ TiO$_2$ system [4].

The present study investigated the chemical resistance to hydrochloric acid instead of the resistance to water studied in [1]. In spite of this, certain regularities are clearly observed: the smallest decrease in the film thickness after etching (i.e., the highest chemical resistance, in accordance with the adopted method of evaluation [1]) is registered in films 1, 3, and 7, regardless of the mass content of film-forming oxides in the FFS. These coatings have the greatest submicrohomogeneity. Coatings 2 and 4 in series B are destroyed to a somewhat lesser extent than their analogs in series A. For the other coatings no differences were observed.

An x-ray phase analysis of powders made of solutions with a different mass content of film-forming oxides (Table 2) shows that they differ not only quantitatively but also qualitatively. The quantity of crystals of bismoxlite BiOCl, present in all samples (regardless of the initial solution concentration), is minimum in powder 3 and gradually increases in going to powders 1 and 7 in series B. Ferric chlorides are present in samples 2, 3, and 4 of the same series, their quantity being maximum in powder composition 3 and somewhat smaller in samples 2 and 4.

If the total molar content of the film-forming oxides in the solutions is equal to 2.5% (series A), the bismoxlite content in the powders increases twice: from 29 to 137 and from 101 to 142 arb. units in transition from composition 1 to 4 and from 5 to 7, respectively. Ferric chloride is identified in the first two samples in series A, and a crystalline phase with a spinel structure is present in powders 3 – 6. No crystals of this composition are registered in powders of series B.

The observed differences can be related to inadequate conditions of powder preparation. The powders were dried at a temperature of 80°C, but when the mass content of oxides

in the FFS was decreased from 5 to 2.5%, the heat-treatment duration was increased by about 20%. Hence, the powders were obtained under nonequilibrium conditions, and the degree of equilibrium increases with increasing duration of the drying, i.e., as the total mass content of film-forming oxides in the solution decreases.

The degree of nonequilibrium of the process of melting and annealing has a significant effect on the crystalline phases identified in the glass: the first crystallizing phases are metastable phases whose structure is close to a vitreous structure and whose formation involves overcoming the lowest energy barriers [5]. The FFS were prepared using iron and bismuth chlorides, and therefore, they are identified in all the powders. To form crystals of a complex chemical compound with a spinel structure, a certain excess energy is needed, and an increase in the degree of equilibrium of the powder preparation process facilitates accumulation of this energy. Moreover, the size of the sol particles (and the melting point, solubility, and chemical activity of the disperse phase, which depend on this size) is determined by the solution concentration and has a substantial effect on the reactions taking place in the powders and films.

As could be expected, the submicrostructure of the films depends strongly on the total mass content of film-forming oxides in the FFS (Fig. 1).

The variation in the submicrostructure of powders of series B correlates with the viscosity of the corresponding solutions, namely, an increase in the microinhomogeneity correlates with increased viscosity, i.e., the structural specifics of the sol-gel films are determined in the stage of FFS preparation and are largely determined by the degree of FFS dispersion [1].

The refractive index of films 1 – 6 in series B is constant within the limits of experimental error, and that of film 7 is somewhat lower. The specular-reflection coefficient is in direct proportion to the refractive index.

The microhardness of all films in series B is virtually the same, and is higher only in film 2, which is probably determined by the formation of chain-shaped submicrostructures. A small quantity of such inclusions is identified in coating 3. The formation of these microstructures correlates with the presence of TiO$_2$ crystals in powder 2, heat-treated at a temperature up to 400°C. An increase in the temperature to 950°C fosters the beginning of TiO$_2$ crystallization in powder 3.

The chemical resistance of films 1, 3, and 7 appears to be higher (the decrease in the coating thickness after etching is smaller) than in the other films in series B. This is presumably related to the degree of structural inhomogeneity.

In general, the relationship between the composition and properties of the considered coatings is less clearly manifested than in analogous films of series A and is probably due to the increased nonequilibrium of the physicochemical processes in powder preparation and film synthesis.

Table 3 shows the variations in the viscosity of FFS and the properties of films of series B in relatioon to the age of the deposited FFS.

The solutions of compositions 3 – 7 exhibited finely crystalline precipitates consisting of oxides of film-forming components. The experiments showed that the appearance of sediments in FFS with a total mass content of film-forming oxides equal to 2.5% is accompanied by an increase in the relative fraction of Bi_2O_3 in the solution (compared to freshly prepared FFS), i.e., the sediment consists mostly of compounds iron and titanium. One can assume that similar processes take place in the formation of sediments in FFS with a higher mass content of film-forming oxides. This is corroborated by the increased amount of bismoxlite in powders made of a 27-day solution of composition 3 and a 79-day solution of composition 4, compared to the x-ray phase data of identical powders made of freshly prepared solutions (Tables 2 and 3). Hence it follows that the solutions have a lower content of the polymer-forming component (titanium dioxide). This degrades the continuity of the coatings and increases the light scattering, which leads to a decrease in the specular-reflection coefficient in films 3 – 7 (Tables 1 and 3).

It can be assumed that the viscosity of the FFS will decrease immediately after the appearance of the precipitate [2, 6], and the content of the coarsely disperse phase in the FFS and, consequently, the size and number of inclusions in the films should decrease. This is corroborated by the fact that the submicrostructure of the coatings improves perceptibly (Fig. 1a and 2). The viscosity of solutions 4 – 7 is lower than that of freshly prepared ones. An exception from this regularity is FFS 3 and film 3. The viscosity of the 79-day solution is higher, the number of inclusions in the coating increases, and the submicrostructure is significantly degraded.

This can have the following explanation. After the formation of the precipitate, the total mass content of the film-forming oxides in the FFS decreases, and the relative content of Cl ions and water introduced into the colloidal system with alcohol, hydrochloric acid, and ferric chloride crystallohydrate increases. This intensifies the agglomeration processes, which leads to increased viscosity of the FFS and coarsening of the coating microstructure.
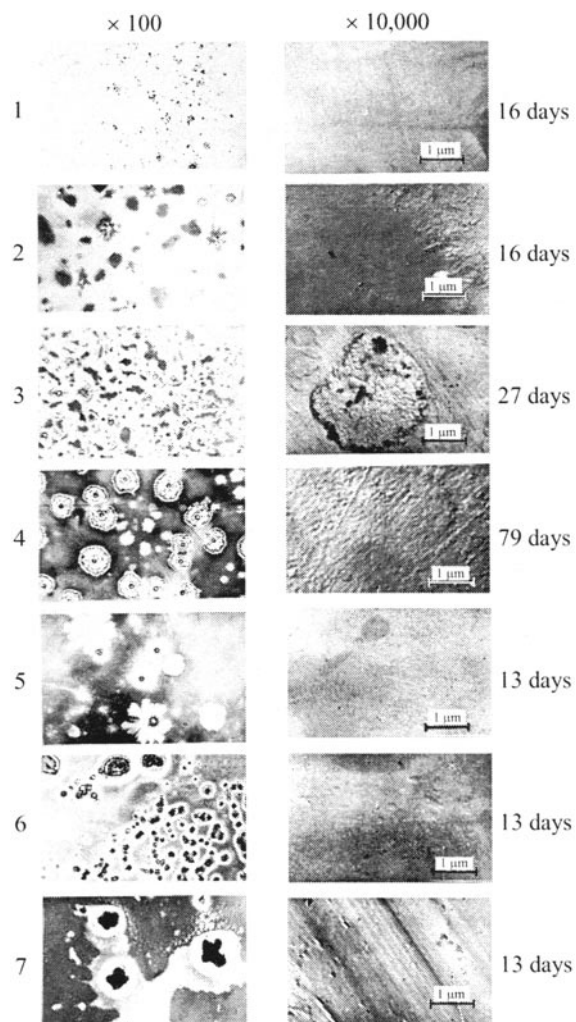

Fig. 2. Films of series B made of solutions of different ages.

No precipitate was formed in solutions 1 and 2; however, their viscosity is lower than that of freshly prepared solutions. The reason for this, in our opinion, is the tendency of colloidal FFS toward stabilization, which is manifested in a coarsening of the disperse phase to sizes commensurable with the resolution of a light microscope (composition 1) and in "curling" of the chain formations (composition 2). The

TABLE 3

| Sample | Molar content of Bi_2O_3, % | FFS | | Distribution confidence interval | | | X-ray phase analysis data, arb. units |
		viscosity, mm^2/sec	age, days	refractive index	specular-reflection coefficient, %	microhardness, MPa	
1	10	2.31	16	2.210 – 2.176	42.3 – 41.1	7000 – 6830	–
2	20	2.23	16	2.154 – 2.090	35.1 – 34.8	6720 – 6507	–
3	30	2.46	27	2.116 – 2.058	36.4 – 31.4	6701 – 6495	BiOCl – 47, $FeCl_3 \cdot H_2O$ – 38
4	40	2.30	79	2.045 – 1.915	26.4 – 25.0	6785 – 6493	BiOCl – 118
5	50	2.58	13	1.987 – 1.893	20.4 – 18.5	6441 – 5492	–
6	60	2.64	13	1.902 – 1.772	23.2 – 18.2	6249 – 5997	–
7	70	2.64	13	1.899 – 1.773	15.9 – 13.9	6205 – 5721	–

submicrostructure of the films also undergoes changes: chain forms appear in coating 1, and in film 2, on the other hand, chain forms disintegrate.

No perceptible effect of the age of the solution on the refractive index of the coatings was registered within the limits of experimental error. The maximum value of the Vickers microhardness was observed in film 1, which is in accordance with the microstructural transformations.

Thus, the inadequacy of the physicochemical processes taking place in FFS with different total mass content of the film-forming oxides results in different structures and properties in coatings with identical compositions. With increasing oxide content, the nonequilibrium of the physicochemical processes in the solutions, powders, and films is intensified. An increase in the content of film-forming oxides increases the solution viscosity, intensifies the propensity of the films toward the formation of large inclusions, and makes the submicrostructure coarser.

The studies revealed a clear relationship between the submicrohomogeneity of the films and the viscosity of the FFS, between the increase in the microhardness and the formation of chain structures, and between the improvement in the submicrohomogeneity and the increased chemical stability. As the solution ages, its viscosity and the properties of the coating change regularly, which is related to structural transformations and the appearance of a precipitate.

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